BIOMETHANATION OF PALM OIL MILL EFFELUENT (POME) BY ULTRASONIC MEMBRANE ANAEROBIC SYSTEM (UMAS) USING POME AS SUBSTRATE

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Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (Technology Gas)

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JANUARY 2014

ABSTRACT

The direct discharge of the Palm Oil Mill Effluent (POME) wastewater causes serious environmental pollution due to its high chemical oxygen demand (COD), total suspended solid (TSS) and biological oxygen demand (BOD). The conventional ways for POME wastewater treatment have both economical and environmental disadvantages. In this study, the potential of ultrasonic-assisted membrane anaerobic system (UMAS) was evaluated as alternative and cost effective method for treating POME wastewater to avoid fouling. The UMAS treatment efficiency was greatly improved by UMAS introduction. The membrane fouling and polarization at the membrane surface was significantly reduced. This research had proved that UMAS is the effective way to treat POME. The removal efficiency of COD was 95% with HRT of 6 days. The BOD removal efficiency was 71.59% while TSS removal rate was from 91 to 99.5%.The methane gas production efficiency was 94.14%.The UMAS treatment efficiency was greatly improved by UMAS introduction. The membrane fouling and polarization at the membrane surface was significantly reduced. This research had achieved the objectives by resolve the problem statement.

Key words: UMAS, Anaerobic, POME, COD, membrane, ultrasonic

ABSTRAK

Pelepasan air pemprosesan kelapa sawit (POME) tanpa rawatan akn menyebabkan pencemaran kerana ia mengandungi keperluan oksigen kimia (COD), keperluan oksigen biologi (BOD) dan jumlah pejal (TSS) yang tinggi. Rawatan konventional bukan sahaja memerlukan kos yang tinggi juga menyebabkan pencemaran. Dalam kajian ini, potensi kaedah rawatan dengan sistem membran anaerobik berultrasonik (UMAS) dikaji supaya dijadikan pilihan alternative dan kaedah kos efektif untuk rawatan air pemprosesan kelapa sawit dan mengelakkan masalah membrane tersumbat. Kecekapan sistem rawatan UMAS ditingkat dengan ultrasonik yang dipasang. Masalah membrane tersumbat dan polarasi didapati berkurangan. Kajian ini telah membuktikan bahawa UMAS adalah cara yang berkesan untuk merawat POME. Kecekapan penyingkiran COD adalah 95% dengan HRT 6 hari. Kecekapan penyingkiran BOD adalah 71,59% manakala TSS kadar penyingkiran adalah 91-99,5%. Kecekapan pengeluaran gas methana adalah 94,14%. UMAS menunjukkan keberkesanannya rawatan telah bertambah baik dengan pengenalan UMAS. Ini kejadian membran tersumbat dan polarisasi di permukaan membran telah dikurangkan dengan ketara. Kajian ini telah mencapai objektifnya berdasarkan menyelesaikan pernyataan masalah.

Kata kunci : UMAS, Anaerobik, POME, COD, membran, ultrasonik

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LIST OF SYMBOLS

<	less than
=	equal
%	Percentage
$^{\circ}$C	Degree Celsius
P	Pressure
T	Temperature

LIST OF ABBREVIATIONS

BOD	Biological Oxygen Demand
CDM	Certified emission reduction
CER	Clean development mechanism
CO_2	Carbon dioxide
COD	Chemical Oxygen Demand
CUF	Crossflow Ultrafiltration
Da	Dalton
GHG	Green House Gases
GFTS	Green Technology Financing Scheme
HRT	Hydraulic Retention Time
IR	Infrared
NaOH	Sodium hydroxide
MAS	Membrane Anaerobic system
MLSS	Mixed liquor suspended solid
MPOB	Malaysian Palm Oil Board
MWCO	Molecular cut off
OLR	Organic Loading Rate
POME	Palm Oil Mill Effluent
PVC	Polyvinyl chloride
RO	Reverse Osmosis
SRT	Solid Retention Time
SS	Suspended Solid
TPAD	Temperature phase anaerobic digester
TSS	Total Suspended Solid
UF	Ultrafiltration
UMAS	Ultrasonicated Membrane Anaerobic System

US	Ultrasonic
VFA	Volatile fatty acid
VSS	Volatile Suspended Solid
VS	Volatile Solid
W/W	Weight to weight

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CHAPTER 1

INTRODUCTION

1.1. BACKGROUND OF STUDY

The growth of the palm industry in Malaysia has been phenomenal. Indonesia and Malaysia are the two largest oil palm producing countries (Table 1) and is rich with numerous endemic, forest-dwelling species. Malaysia has a tropical climate and is prosperous in natural resources. Oil palm currently occupies the largest acreage of farmed land in Malaysia (Arif, 2011). While the oil palm industry has been recognized for its contribution towards economic growth and rapid development, it has also contributed to environmental pollution due to the production of huge quantified of by-product from the oil extraction process. The waste products from oil palm processing consist of oil palm trunks (OPT), oil palm fronds (OPF), empty fruit bunches (EFB), palm pressed fibers (PPF) and liquid discharge palm oil mill effluent (POME) (Yusoff, 2007).

Table 1: World Major Producers of Palm Oil 2002-2011 ('000 Tonnes)

Country	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
Indonesia	9,370	10,600	12,380	14,100	16,070	17,420	19,400	21,000	22,100	23,900
Malaysia	11,909	13,355	13,976	14,962	15,881	15,824	17,734	17,565	16,994	18,911
Thailand	600	690	735	700	860	1,050	1,300	1,310	1,380	1,530
Nigeria	775	785	790	800	815	825	840	870	885	900
Colombia	528	527	632	673	714	733	778	802	753	965
Ecuador	238	262	279	319	352	396	410	429	380	460
Papua New Guinea	316	326	345	310	365	382	465	478	500	525
Cote d'Ivoire	265	240	270	290	281	289	285	345	330	310
Honduras	126	158	170	237	258	265	278	280	275	278
Brazil	118	129	142	160	170	190	210	240	250	270
Costa Rica	128	155	180	181	189	200	202	220	230	250
Guatemala	86	85	87	92	125	130	185	180	182	193
Venezuela	55	41	61	63	66	70	89	84	75	77
Others	895	906	1,131	1,065	1,113	1,057	1,092	1,308	1,524	1,611
TOTAL	**25,409**	**28,259**	**31,178**	**33,952**	**37,259**	**38,831**	**43,268**	**45,111**	**45,858**	**50,180**

Source: Oil World Annual (2007-2011) & Oil World Weekly (9 December, 2011)

Palm Oil processing gives rise to highly polluting waste-water, known as Palm Oil Mill Effluent (POME), which is often discarded in disposal ponds, resulting in the leaching of contaminants that pollute the groundwater and soil, and in the release of methane gas into the atmosphere. POME is an oily wastewater generated by palm oil processing mills and consists of various suspended components. This liquid waste combined with the wastes from steriliser condensate and cooling water is called palm oil mill effluent (POME). Moreover, POME has a very high Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD), which is 100 times more than the municipal sewage. POME is a non-toxic waste, as no chemical is added during the oil extraction process, but will pose environmental issues due to large oxygen depleting capability in aquatic system due to organic and nutrient contents (Zafar, 2013). Malaysian experiences in effluent control in the palm oil industry demonstrate that a set of well designed environmental policies can be very effective in controlling industrial pollution in a developing country. The Environmental Quality (prescribed Premises)(Crude Palm Oil) Regulation 1977, promulgated under the enabling powers of

Section 51 of the EQA, are the governing regulations and contain the effluent discharge standards. Other regulatory requirements are to be imposed on individual palm oil mills through condition of license according to Environmental Quality Act 1974 (Pierzynski, 2005). In order to reach the requirement of standard discharge limit, POME treatment can never to be dismissed. It incurs high non-profitable cost in an industry to resolve this problem either the waste water have to be reduced or treatment have to be enhanced in cost effective way.

Instead of treatment system such the conventional ponding system, the membrane anaerobic system (MAS) will be proposed to be utilized. The system consists of two technologies which are anaerobic digestion and membrane technology. Anaerobic digestion is widely adopted in the industry as a primary treatment for POME. Biogas is produced in the process in the amount of 20 m^3 per ton FFB. This effluent could be used for biogas production through anaerobic digestion. At many Palm-oil mills this process is already in place to meet water quality standards for industrial effluent. (Zafar, 2013). With the addition of application of membrane filtration in the system, the efficient of wastewater treatment is elevated that is capable of retaining biomass concentration within the reactor and produce high quality effluent. It is proven to be an effective way in separating biomass solid from digester suspension and recycle them to the digester.

Membrane technology is one of the possible technology solutions to treat the high organic content effluent. Membrane treatment is a physical process alternative that is capable of providing a highly efficient treatment, requires minimal energy and does not introduce any additives to the waste system. Among the various membrane processing techniques, ultra filtration presents an attractive option for wastewater treatment. It is a low pressure-driven membrane process retaining most effectively macromolecules sized within 0.001 – 0.02 µm. Membrane ultrafiltration is capable of producing a higher quality effluent that can successfully meet the increasingly stringent effluent discharge standards set out in the Environmental Quality Act, 1974.

However, in this membrane anaerobic system has to be monitored properly as the processes rely solely on the micro-organism to break down the pollutants. The micro-organism is very sensitive to changes in the environment for the micro organism. Besides there will be problem arises in the membrane system due to the characteristic of POME as it has a high suspended solid effluents. The membrane will be suffered from fouling and degradation during use. The process by which a variety of species present in the water increase the membrane resistance, by adsorbing or deposition onto its surface, adsorption onto the pore surface within the bulk membrane material (pore restriction) or by complete pore blocking. (Leonard Lim Lik Pueh, 2004)

1.2 PROBLEM STATEMENT

The main problem statement is POME contains highly organic content of wastewater. Since these compounds are harmful to the environment, it becomes necessary that effluents water should be treated or purified before discharge into the environment. This POME would normally have resulted in significant environmental pollution if discharge directly without efficient treatment being implemented. Coming to the context of water and air pollution, POME is one of the agriculture waste blame on.

Greenhouse gasses emitted from Palm Oil Mill Effluent anaerobic treatment pond such as methane and carbon dioxide exerted greenhouse effect to the earth. The capturing of methane gas will save the environment. Besides, the treatment of POME often incurs high non-profitable cost is an industries that reduces the company profit. In addition, the cost of fossil fuel increases with the increasing demand and the depleting resource making it even valuable. The concept of transforming waste to energy makes waste treatment seem more appealing and cost-effective.

Besides, membrane technology that applied in the efficient treatment of POME to be monitored properly because there will be problem arises in the membrane system due to the characteristic of POME as it has a high suspended solid effluents. The membrane will be suffered from fouling and degradation during use it continuously in industry scale. The study should be conducted to overcome all the problems arise in treatment of POME.

1.3 OBJECTIVES OF THE STUDY

The research aims to solve the problem statement by accomplishing the following specific objectives:

1. To enhance the treatability of high concentrated POME by Ultrasonic membrane anaerobic system (UMAS)
2. To study the membrane fouling control and increment of methane gas by application of Ultrasonic membrane anaerobic system (UMAS)
3. To evaluate the overall performance of Ultrasonic membrane an aerobic system (UMAS) in treating Palm Oil Mill Effluent (POME)

1.4 SCOPE OF RESEARCH

This study is focused on enhance the treatability of using UMAS for treatment of highly concentrated of POME. The system performance were evaluated with significant parameter such as COD, BOD, TSS, and VSS for the raw material, material in the reactor and the treated permeate to observe the efficiency of the system. In order to optimize the production of methane and overcome membrane fouling problem, a 150 L bioreactor system and cross flow membrane module is attached with ultrasonic device. The parameters such as pH and temperature are controlled and maintain in optimum operating condition.

1.5 RATIONALE AND SIGNIFICANT

As the palm oil industry require tackling the challenges in meeting the growing worldwide demand for palm oil as food, while at the same time has to demonstrate the sustainability of its products and operations. The issue of environmental pollution should be concern to maintain the sustainability of palm oil industry. Realizing the danger of the possible directly discharge of POME, the study will provide some efficient way in treating the POME by reducing the organic content of POME and reducing the emission of green houses gasses to the environment. The study can protect the environment from pollution effect of POME.

Besides, with the increasing awareness on the environmental issues and the rising oil prices, all governments across the world are forced to looking for alternative energy, the same phenomenon happen in Malaysia as well. The Renewable energy has been recognized as the country's fifth fuel under the 8^{th} and 9^{th} Malaysia Plan. So, this study can suggest by providing an alternative renewable energy that can be apply in the industry in return overcome the dependency on fossil fuel which is incurs high cost. Eventual, the cost for POME treatment can be reduced and provide alternative energy, it will support Malaysia Plan in the same time it will attract foreign investor without realized.

CHAPTER 2

LITERATURE REVIEW

2.1 PALM OIL MILL EFFLUENT (POME)

POME is generated as a result of sterilization of fresh palm oil fruit bunches, clarification of palm oil and effluent from hydro cyclone operation. (Borja et al, 1996) POME is a high strength agro-industrial polluter due to high value of COD and BOD.POME is in a form of highly viscous dark brown colloidal with fine suspended solid. POME colloidal suspension of 95-96% water, 0.6-0.7% oil and 4.5% total solids (Ma, 1993). The characteristic of POME are shown in **Table 2.1**. In 1980, Malaysian mills discharged 6 million tonnes of effluent which contain equivalent BOD as load generated by population of 7.3 million. However it's highly amendable by anaerobic digestion.

Table 2.1: Characteristic of untreated POME

Parameter	Concentration
pH	4.7
Temperarture	80-90
BOD 3-day, 30˚C	25,000
COD	50,000
Total soilids	40,500
Suspended solids	18,000
Total volatile Solids	34,000
Ammoniacal-Nitrogen	35
Total Nitrogen	750

*All parameter in mg/l except pH and temperature (˚C)

Source: (A.L Ahmad, 2003)

2.2 METHANE GAS FOR ELECTRICITY GENERATION

The generation of electricity from methane is possible, in all cases the steps that must be gone through are twofold, chemical energy to mechanical energy, and then from mechanical energy to electrical energy. For these conversion processes to be achieved, suitable engine is needed, and in principle there are two types of engine which have been used for biogas digester electricity generation that is gas engine and steam turbine.

According to the Malaysia Palm Oil Board (MPOB), 0.65 m3 POME is generated from every processed ton of Fresh Fruit Bunch. Based on a study of the potential for electricity generation from POME that have done by MPOB, if there was 38,870,000 m_3 of POME produced for every 59,800,000 tons of Fresh Fruit Bunches process annually. The annual energy content of the generated methane gas can be calculated to 7.07E+09 kWh. Based on a conversion efficiency of 38 percent (gas engine), the potential annual electrical power generation would be 2.69E+09 kWh. Thus, Palm Oil Mill Effluent has a huge potential for power generation (N.A Ludin et al, 2006).

2.3 POME TREATMENT

2.3.1 Ponding System/Lagoon system/Open Digester tank

Ponding system is the most common system employed in Malaysia which counted for 85% of the total treatment plant in Malaysia. In a ponding system it is basically divided into de-oiling pond tank, acidification ponds, anaerobic ponds and facultative pond or aerobic ponds. The discharge after the facultative or aerobic require further reduce of BOD to comply with the discharge standards. The typical size of the ponding system is equivalent to half a soccer field which is able to sustain the processing capacity of 54 tons per hour. This method is favored due to it can achieve reasonable degree of treatment with low construction and operating cost and is easily maintained as the technology employed is relatively unsophisticated. However, a large land space is required. Direct emission of gasses generated in the treatment process will impose green house effect to the environment. Besides, the effectiveness in meeting the stringent standard is unsatisfactory. (Poh P.E et al, 2009)

Open digester tank are used for POME treatment when limited land area is available for ponding system. Apart from that, in the investigation by Yacobs et al (2006), he proved that anaerobic system emitted higher amount of methane compare to the open digester tank with an average methane composition of 54.4% compare to open digester tank. (Poh P.E et al, 2009)

2.3.2 Anaerobic Digestion

A biochemical process is organic matter is decomposed by bacteria in the absence of oxygen, producing methane and other by products. It's much depends on the bacterial consortia for degradation process, thus a longer time is require. The condition is also required to be always in the optimum condition for the bacterial to survive, as the bacterial are sensitive. However, anaerobic digestion is widely used to treat waste as it require low energy, high organic removal rate, low sludge production and production of methane as valuable by product. (Poh, P.E. et al, 2009)

The degrading process of POME consists of four stages that is hydrolysis and acidogenesis, fermentation, acetogenesis, methanogenesis (Poh, P.E et al,2009). In the first stage of hydrolysis, the polymeric organic materials are hydrolysed to its constituent such as glucose, fatty acids and amino acids by hydrolytic bacteria. The hydrolysis process is of significant importance in high organic waste and may become rate limiting. Solubilisation involves hydrolysis process where the complex organic matter is hydrolysed into soluble monomers. Fats are hydrolysed into fatty acids or glycerol; proteins are hydrolysed into amino acids or peptides while carbohydrates are hydrolysed into monosaccharides and disaccharides.

In fermentation stage, the hydrolysed products are converted to volatile fatty acids, alcohols, aldehydes, ketones, ammonia, carbon dioxide, water and hydrogen by the acid-forming bacteria. The organic acids formed are acetic acid, propionic acid, butyric acid and valeric acid. Volatile fatty acids with more than four-carbon chain could not be used directly by methanogens (Wang et al., 1999).

The following stage is acedogenesis, where organic acids are further oxidised to acetic acid and hydrogen and carbon dioxide which are used in the subsequent process. Acetogenesis also includes acetate production from hydrogen and carbon dioxide by acetogens and homoacetogens.The transition of the substrate causes the pH of the system to drop which beneficial to acidogenic and acetagenic.(K.M Ostrem et al,2004)

Finally the reaction come across the the stage of methanogenesis. One is conversion of acetate to carbon dioxide and methane by acetotrophic organisms and another is reduction of carbon dioxide with hydrogen by hydrogenotrophic organisms. (Ling,L.Y, 2007).

Typical reaction of anaerobic digestion:

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH+CO_2 \qquad [1]$$

$$C_2H_5OH+CO_2 \longrightarrow CH_4+ 2CHOOH \qquad [2]$$

$$CH_3COOH \longrightarrow CH_4 + CO_2 \qquad [3]$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \qquad [4]$$

The advantages of adopting anaerobic system are low energy requirement as no aeration needed. Methane is produced as a valuable end product and generates sludge that could be used for land application. There are several anaerobic treatment method that have been widely used such as Anaerobic filtration, fluidized bed reactor, up-flow anaerobic sludge blanket reactor (UASB), Up flow anaerobic sludge fixed-film reactor (UASFF), continuos stirred tank reactor and Anaerobic contact process. Although these high rate or hybrid reactors are successfully shortened the retention time and efficiency (as shown in table) but all these biological treatment systems need proper maintenance and monitoring as the processes solely rely on micro-organisms to degrade the pollutants. How to ensure the stability of the system deserves most urgent concern. (Y.J Zhang et al, 2007) .The summary of comparisons of all other method are shown in table 2.2.

Table 2.2: Comparisons of various treatment methods on POME treatment

Table 6

:e of various anaerobic treatment methods on POME treatment

	OLR (kg COD/m^3day)	Hydraulic retention time (days)	Methane composition (%)	COD removal efficiency (%)	Reference
Anaerobic pond	1.4	40	54.4	97.8	Yacob et al. (2006a)
Anaerobic digester	2.16	20	36	80.7	Yacob et al. (2005)
Anaerobic filtration	4.5	15	63	94	Borja and Banks (1994b)
Fluidized bed	40.0	0.25	N/A	78	Borja and Banks (1995b)
UASB	10.63	4	54.2	98.4	Borja and Banks (1994c)
UASFF	11.58	3	71.9	97	Najafpour et al. (2006)
CSTR	3.33	18	62.5	80	Tong and Jaafar (2006)
Anaerobic contact process[a]	3.44	4.7	63	93.3	Ibrahim et al. (1984)

N/A: data unavailable.
[a] In terms of BOD.

Source: (Poh P.E et al, 2009)

2.3.3 Membrane Separation Technology

Membrane Separation technology is always employed in waste treatment as it's able to produce consistent and good water quality after treatment plants as well as it's able to disinfect the treated water. There have been inspiring performances by using membrane separation technology. For instances, A.L Ahmad et al (2003) have shown that the combination of UF & RO is able to achieve COD removal of 98.8%,BOD removal of 99.4%, Turbidity of 100% and pH 7 as a result. Another group of researcher have incorporated Hollow fiber membrane in their three phase decanter system to give 89.9% COD removal, 99.4% of TSS elimination, 97.9% Turbidity reduction and 92.9% for color removal (S.S Raja et al, 2005).However, short membrane life, membrane fouling and expensive cost are major constraint of this technique. In order to prolong the membrane life span and produce crystal clear effluent as well as methane as the end product, the integration of anaerobic system and membrane separation technology in a bio reactor is investigated by some researchers.

2.3.4 Membrane Anaerobic System

The idea of integration of the anaerobic digestion system and membrane separation technology is to enable the biomass to be retained in the reactor which improves methane gas emission as well as producing constant high quality effluent. According to Y.J Zhang et al in 2007 she has incorporating Expanded Granulated Sludge Blanket (EGSB) with UF & RO. As a result, COD Removal of 93%, biogas conversion rate of 43% is achieved. As we compared the result to the previous table, the biogas generation appears to improve drastically. In the later years, H.N Abdurahman et al (2011) have shown another more inspiring result by his Membrane Anaerobic System which a design of anaerobic bioreactor equipped with UF module membrane where COD Removal efficiency 96.6%-98.4% and biogas conversion rate up to 73% as a final result.

However, although the membrane fouling problem may relief compared to the case without anaerobic digestion as pretreatment but the membrane fouling problems still an issues and the idea of back flushing membrane which require an operation break is not feasible to the industrial application. Hence, as a solution application of ultrasonic technology in solving the membrane fouling problem is going to be investigated in this research work.

2.4 METHANOGENS

Methanogen are specialized group of Archae that utilized a limited number of substrates, principally acetate, carbon dioxide and hydrogen for methane production or methanogenesis. These substrate resulted from the degradation from more complex substrate. Methane-forming bacteria have many shapes (bacillus, coccus, and spirillum), sizes (0.1 to 15μm), and growth patterns (individual cells, filamentous chains, cubes, and sarcina). Methane-forming bacteria are oxygen-sensitive anaerobes and are found in habitats that are rich in degradable organic compounds. In these habitats oxygen is rapidly removed by bacterial degradation of the organic compounds.